Radiaire seleniumverbindingen met silicium, germanium en tin als centrale atomen

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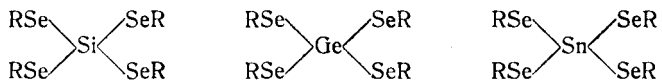
VIII. SUMMARY.

This thesis describes the esters of tetraselenoorthosilicic acid, tetraselenoorthogermanic acid and tetraselenoorthostannic acid:



The aromatic selenols, needed for the preparation of these esters, were prepared by treating the arylmagnesium bromides with selenium and decomposing the intermediate products with cold hydrochloric acid.

A simple method was elaborated for the preparation of the aromatic and hydroaromatic esters of *tetraselenoorthosilicic acid.* Silicium tetrachloride was made to react with a suspension of the sodium selenomercaptides in toluene, which were obtained by heating the selenols with sodium in toluene.

In this way the phenyl, p.tolyl, p.tert.butylphenyl, p.chlorophenyl and cyclohexyl esters were prepared. The esters are crystalline, colourless products. The phenyl ester gives rhombic, the cyclohexyl ester tetragonal crystals.

For the preparation of the aromatic and hydroaromatic esters of *tetraselenoorthogermanic acid,* two methods were elaborated, viz.:

1. Reaction of germanium tetrachloride with a suspension of sodium selenomercaptide in toluene.
2. Reaction of germanium tetrachloride with arylselenium-magnesium bromide in ether.

The first method is the best. In this way the phenyl, p.tolyl, p.isopropylphenyl, p.tert.butylphenyl, p.chlorophenyl, α-naphtyl and cyclohexyl esters were prepared.

Only the phenyl ester was also prepared by the second method.

The esters are well crystallizing, yellow products. The crystallo-

graphic properties of the phenyl (tetragonal?), p.chlorophenyl (rhombic, pseudo tetragonal) and cyclohexyl (monoclinic) esters were examined.

The tetracyclohexyl ester of tetrathioorthogermanic acid exists in two enantiotropic modifications; a tetragonal form, stable at room temperature, changes at 68.5° into a monoclinic form.

The tetracyclohexyl ester of tetraselenoorthogermanic acid shows only the monoclinic form, which closely resembles the monoclinic modification of the sulfur compound.

For the preparation of the tert.butyl ester germanium tetrachloride was made to react with tert.butylseleniummagnesium chloride. This ester shows the characteristic properties of „filled molecules".

The reaction of germanium tetrachloride with tert.butyl mercaptide gives a mixture containing the tetra-tert.butyl ester and the tri-tert. butyl ester of the monochlorotrithioorthogermanioformic acid, in a ratio of 1 : 2. The formation of the tri-tert.butyl ester of the monochlorotriselenoorthogermanioformic acid was not observed. The steric hindrance is thus diminished.

The aromatic esters of *tetraselenoorthostannic acid* were prepared by the same methods as the esters of tetraselenoorthogermanic acid.

The phenyl, p.tolyl, p.tert.butylphenyl and p.chlorophenyl esters were obtained by the first method, the phenyl and p.tolyl esters also by the second method.

These esters are crystalline, yellow products. The tert.butyl ester was obtained by the interaction of stannic chloride and tert.butylseleniummagnesium chloride.

List of new compounds.

Esters of tetraselenoorthosilicic acid.

		m.p.
$Si(SeC_6H_5)_4$	phenyl	136.5—137°
$Si(SeC_6H_4CH_3)_4$	p.tolyl	128—128.5°
$Si\{SeC_6H_4C(CH_3)_3\}_4$	p.tert.butylphenyl	175—176°
$Si(SeC_6H_4Cl)_4$	p.chlorophenyl	182—183°
$Si(SeC_6H_{11})_4$	cyclohexyl	93.5—94°